Kinetics of the Reaction of Atomic Oxygen with Tetramethylsilane

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The rate constant for $O(2p)^3P_J + (CH_3)_4Si$ has been measured using the flash photolysis/resonance fluorescence technique over the temperature range 380–700 K. The results are described by $k = (5.1 \pm 0.7) \times 10^{-11}$ exp(−24.1 ± 0.6 kJ mol^{-1}/RT) cm^3 s^{-1} where the uncertainties represent ±1σ precision. The 95% accuracy interval for k is about ±15%. The results show that the activation energy E_a is reduced compared to other hydrocarbons by the trimethylsilyl group. A series of O + primary C–H bond reactions are considered, and possible correlations between E_a and the C–H bond energy and hydrocarbon ionization potential are discussed.

Introduction

The flash photolysis/resonance fluorescence (FP–RF) method has been employed to carry out the first investigation of the reaction

$$O + (CH_3)_4Si \rightarrow \text{products} \qquad (1)$$

from 380 to 700 K. The aim is to characterize how substitution of H in CH_4 by a trimethylsilyl group affects the reactivity of the remaining C–H bonds toward atomic oxygen, $O(2p)^3P_J$, for comparison with hydrocarbon reactions.

We are interested in the lability of methyl groups attached to silicon in two contexts. First, it has been established by FP–RF and discharge flow experiments that trimethylsilane is more reactive toward O than silane,[1-3] and possible reaction at the C–H bonds might contribute toward the overall consumption of O. Second, the reaction

$$O + Si_2(CH_3)_6 \rightarrow \text{products} \qquad (2)$$

has been attributed to O atom insertion into the Si–Si bond,[4] and again we would like to quantify the possible C–H bond reactivity. This reactivity might well be greater than in CH_4, because of the C–H bond weakening influence of the $Si(CH_3)_3$ group.[5] The small C–H bond strength, D, in $(CH_3)_4Si$ broadens the range of D in H atom abstraction reactions which have been investigated and thus permits a correlation of the activation energy with D.

Experimental Technique

Tetramethylsilane (Aldrich, 99.9+%) was degassed by freeze–pump–thaw cycles, and other materials were used as described earlier.[2] The reactor and general FP–RF method have been discussed previously,[6,7] as well as details of the generation and detection of atomic O.[2] In summary, O atoms are formed by flash photolysis of a precursor, either O_2 or SO_2 here, and are monitored by time-resolved atomic resonance fluorescence at a wavelength of 130 nm.[8] The fluorescence is excited by a microwave-powered discharge lamp and is observed through magnesium fluoride optics with a solar-blind photomultiplier tube. Current pulses from individual photons are amplified and then counted by a computer-controlled multichannel scaler.

After generation in the reaction zone O atoms are lost over 1–100 ms because of (i) reaction 1 and (ii) diffusion and recombination with the precursor, described by k_{diff}. The experiments were carried out in a large excess of Ar bath gas to maintain thermal equilibrium and to slow diffusive losses. Because diffusion of O to the walls of the reactor is slower than consumption by chemical reactions, the reaction zone is effectively wall-less.

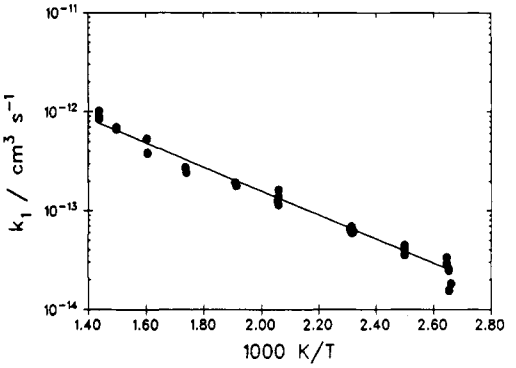

Figure 1. Arrhenius plot for the reaction O + $(CH_3)_4Si$.

The temperature, T, of the reaction zone is measured at the beginning and end of each experiment with a thermocouple previously corrected for radiation errors. The uncertainty in T is estimated conservatively to be $\sigma_T/T \approx 2\%$. An experiment involves monitoring [O] as a function of time at zero reactant concentration and typically five values of $[(CH_3)_4Si] \gg [O]$, at a constant precursor concentration and a constant total pressure, P, i.e. constant k_{diff}. Under these pseudo-first-order conditions

$$[O] = [O]_0 \exp(-k_{ps1}t) \qquad (3)$$

where t is the time after the photolysis flash and k_{ps1} is the pseudo-first-order decay constant:

$$k_{ps1} = k_1[(CH_3)_4Si] + k_{diff} \qquad (4)$$

k_{ps1} is obtained by nonlinear least-squares fitting to the fluorescence decay traces,[9] and k_1 and its statistical uncertainty σ_{k1} are obtained from the slopes of weighted linear plots[10] of k_{ps1} vs $[Si(CH_3)_4]$, with all other conditions held constant.

Results

Preliminary checks showed that no fluorescence is detected in the absence of added O atom precursor, i.e. no fluorescence that might interfere with the experiments is excited from any photolysis fragments of $(CH_3)_4Si$.

Thirty-three measurements of k_1 as a function of T are summarized in Table I, together with the experimental parameters P, flash lamp discharge energy F, precursor type and concentration, and the gas residence time within the reactor before photolysis, τ_{res}. The data at 377 K are the most scattered (with a standard deviation of about 23% of k_1), which might reflect the influence of some or all of the following: secondary chemistry,

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TABLE I: Summary of Rate Constant Measurements for O + $(CH_3)_4Si$

T, K	P, mbar	τ_{res}, s	F, J	$[O_2]$, 10^{16} cm^{-3}	$[SO_2]$, 10^{15} cm^{-3}	$[(CH_3)_4Si]_{max}$, 10^{15} cm^{-3}	$k_1 \pm \sigma_{k1}$, 10^{-14} cm^3 s^{-1}
376	133	1.0	4.05		5.81	3.05	1.82 ± 0.04
377	66.7	1.0	1.25		5.83	3.07	1.56 ± 0.04
377	66.7	1.0	2.45		5.83	3.07	2.49 ± 0.05
377	66.7	1.0	5.00		5.83	3.07	2.56 ± 0.10
378	68.0	1.0	2.45	1.54		3.06	2.85 ± 0.45
378	66.7	2.0	4.05		5.96	3.13	2.86 ± 0.06
378	100	2.0	4.05		6.08	3.18	2.92 ± 0.18
378	133	2.0	4.05		6.15	3.22	3.36 ± 0.11
400	66.7	1.0	2.45		5.43	1.62	3.55 ± 0.36
400	66.7	1.0	4.05		5.43	1.62	4.44 ± 0.28
400	66.7	1.0	5.00		5.43	1.62	4.02 ± 0.08
431	133	1.0	4.05	1.13		1.65	6.01 ± 0.51
432	68.0	1.0	2.45	1.02		1.49	5.95 ± 1.14
432	68.0	1.0	5.00	1.02		1.49	6.86 ± 0.46
431	133	1.0	4.05		4.80	1.33	6.21 ± 0.44
433	66.7	1.0	4.05		4.75	1.31	6.47 ± 0.14
486	66.7	0.5	4.05	0.60		1.34	13.8 ± 1.7
486	133	1.0	4.05	0.61		1.32	11.5 ± 0.2
486	135	3.0	4.05	0.63		1.97	16.3 ± 0.4
487	66.7	1.0	4.05		4.57	1.33	12.6 ± 0.4
523	133	1.0	4.05		4.24	1.24	18.0 ± 1.6
524	68.0	1.0	4.05		4.29	1.25	19.3 ± 1.7
575	66.7	2.0	4.05		3.44	1.04	24.6 ± 1.4
576	101	0.9	4.05		3.35	0.86	27.3 ± 0.6
576	101	3.0	4.05		3.83	0.96	27.5 ± 1.0
623	201	1.0	4.05		3.54	0.48	38.3 ± 1.9
624	101	1.0	4.05		3.22	0.47	52.9 ± 2.9
668	133	1.0	4.05		3.36	0.53	66.6 ± 6.1
668	66.7	1.0	4.05		3.33	0.53	69.2 ± 6.0
696	66.7	0.5	4.05		2.15	0.33	101 ± 2
696	133	1.0	4.05		3.23	0.32	84.7 ± 4.2
696	133	2.9	4.05		3.08	0.43	88.3 ± 2.3
696	68.0	2.1	4.05		3.24	0.31	87.3 ± 4.3

uncertainty in T (which could in the worst case contribute ±16% to the uncertainty of the temperature-dependent k_1 values), and possible surface adsorption of $(CH_3)_4Si$ at the reactor walls. The first factor is considered in more detail at the low end of the temperature range where k_1 is smallest and the measurements are most vulnerable to secondary chemistry such as reaction of O with reaction or photolysis products. While absolute $[O]_0$ cannot be determined in this apparatus (and is not required for finding k_{ps1}), for a given precursor concentration we expect $[O]_0$ to increase with F, and thus examination of k_1 as a function of F tests the extent to which the primary reaction 1 has been isolated from interfering processes. The eight k_1 values at 377 K do not show a significantly consistent variation with F (by contrast, for example, to a previous experiment[11] where a clear trend of the rate constant with F was seen and corrected for by extrapolation to $F = 0$). At higher temperatures there is no consistent variation of k_1 with P, F, precursor type, and τ_{res}, which demonstrates that the observed kinetics there are independent of $[O]_0$ and that there is no significant decomposition of the gas mixture at elevated temperatures. The precisions σ_T and σ_{k1} were used to weight $1/T$ and $\ln k_1$ for the Arrhenius plot shown in Figure 1. The fit to the form $A \exp(-E_a/RT)$ is

$$k_1 = (5.1 \pm 0.7) \times 10^{-11} \exp(-24.1 \pm 0.6 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ s}^{-1} \quad (5)$$

for 380 K ≤ T ≤ 700 K, where the uncertainties in A and E_a are ±1σ.[12] Consideration of the covariance, which accounts for coupling between errors in A and E_a,[13] leads to 2σ precision limits for k_1 of ±6% in the middle of the temperature range and ■11% at the extremes. There are apparently no earlier determinations of k_1 against which to check the data for systematic errors, but results obtained with the present apparatus for the reactions of SiH_4 with atomic O,[2] H,[14] and Br[7] are in good accord with most previous determinations. An allowance of ±5% for possible overlooked systematic errors here leads to an approximate 95% confidence interval of ±15% of k_1.

Discussion

The rate constant k_1 and the Arrhenius parameters can be compared with those for some hydrocarbon oxidation reactions:

$$O + CH_4 \rightarrow CH_3 + OH$$
$$k_6 = 9.8 \times 10^{-11} \exp(-42 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ s}^{-1} \quad (6)$$

$$O + C_2H_6 \rightarrow C_2H_5 + OH$$
$$k_7 = 1.8 \times 10^{-10} \exp(-33 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ s}^{-1} \quad (7)$$

$$O + (CH_3)_4C \rightarrow (CH_3)_3CCH_2 + OH$$
$$k_8 = 1.5 \times 10^{-10} \exp(-30 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ s}^{-1} \quad (8)$$

Reactions 6–8 are selected because they are part of a homologous series of reactions of RCH_3 + O where OH is the known product and where all the H atoms have the same chemical environment.[15] The A factors are within a factor of 2 of 1 × 10^{-10} cm^3 s^{-1}, demonstrating a fairly loose transition state for H atom abstraction. The fit for reaction 1 is consistent with these A factors, and OH production is the most reasonable channel. The E_a for reaction 1 is smaller than for reactions 6–8, which might reflect the low C–H bond energy in $(CH_3)_4Si$ of 415 kJ mol^{-1}.[5] Evans and Polanyi proposed a linear relation between the overall enthalpy change ΔH and E_a,[16] which is tested here by a plot of E_a vs D, the C–H bond strength,[17] in Figure 2a. As may be seen, this correlation is obeyed reasonably well, given the experimental uncertainties in D and E_a, which is further evidence that reaction 1 is analogous to the other processes.

The transition state for these abstraction reactions involves a transfer of electron density from the C–H bond being broken to the partially formed O–H bond, and accordingly the energy of the transition state might vary consistently with the ionization potential[1,18] (IP) of RCH_3. This idea is tested by the plot of Figure 2b. There is a reasonable correlation, with a linear

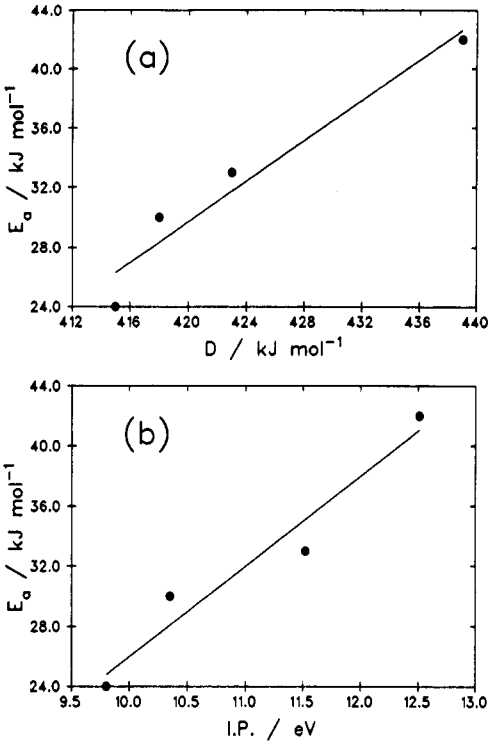

Figure 2. (a) Plot of E_a for C–H abstraction versus C–H bond strength, D. (b) Plot of E_a for C–H abstraction versus ionization potential, IP.

relationship between E_a and IP for the abstraction of H from RCH_3:

$$E_a \approx [6\mathrm{IP/eV} - 34]\ \mathrm{kJ\ mol^{-1}} \quad (9)$$

Provided that further work supports similar relations, e.g. for secondary and tertiary H-atom abstraction, then such relations may be more widely applied than correlations involving D, because reliable IP data are available for a very broad range of hydrocarbons.[18] Combination of the correlations of Figure 2a,b also suggests a correlation of D with IP. Our systematization of E_a for primary H atom abstraction is an alternative approach to that of Cohen and Westberg,[19] who instead proposed a single energy barrier for this process, but with reactions 6 and 7 as exceptions.

Equation 9 can be tested via estimation of E_a for

$$O + (CH_3)_3CC(CH_3)_3 \rightarrow (CH_3)_3CC(CH_3)_2CH_2 + OH \quad (10)$$

from the IP of the alkane of 9.8 eV.[18] The predicted E_a of 25 kJ mol^{-1}, when coupled with an assumed A factor of 1.5×10^{-10} cm^3 s^{-1}, yields k_{10} at 298 K of about 6×10^{-14} cm^3 s^{-1}, which is about a factor of 2 below the experimental value.[20] On the unfavorable assumption that all the error is within E_a, this difference corresponds to an error of only 2 kJ mol^{-1} in E_a and is comparable to the scatter in Figure 2b. Equation 9 suggests that H abstraction from CH_3 groups in silicon-containing alkanes may be easier than previously thought. For example, Hoffmeyer et al.[4] compared their k_2 measurements to k_{10}, but the IP of $Si_2(CH_3)_6$ of 8.27 eV[18] suggests that a smaller E_a for abstraction of around 16 kJ mol^{-1} is likely. Nevertheless, their product studies suggested that insertion dominated over abstraction, although it is possible that abstraction becomes important at elevated temperatures. Similarly, we also consider the reactions

$$O + (CH_3)_3SiH \rightarrow (CH_3)_3Si + OH \quad (11a)$$

$$\rightarrow CH_2(CH_3)_2SiH + OH \quad (11b)$$

If k_{11b} is similar to k_8 then the branching ratio for C–H abstraction $k_{11b}/k_{11a} + k_{11b})$ is about 4×10^{-4} at room temperature.[21] Equation 9 predicts an E_a for abstraction similar to that for reaction 1, which leads to a larger branching ratio of around 2×10^{-3}. Abstraction from the Si–H bond is most likely to be the dominant channel in this case.[1,15]

Conclusions

The rate constant for H atom abstraction from tetramethylsilane has been characterized over the temperature range 380–700 K, and the preexponential factor is of the same order as other O + hydrocarbon reactions, while E_a is lower. Tentative relations between E_a for a series of primary H atom abstraction reactions and the hydrocarbon C–H bond strength or ionization potential have been proposed.

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